TABLE II

Experimental Scouring Data

(Bake Temp = 575F Lard-Chicken Fat Ratio of 80:20)

Scouring agent	Scouring strokes	Scouring eff., relative to A
Steel wool & soap = A	21	100
Steel wool after 8 use cycles	20	105
Silex on nylon = B	41	51
Silex on nylon after 32 use cycles	48	44
Silex on cloth = C	71	30
Steel wool & soap on paper	26	81
Steel wool & soap on sponge	20	105

scouring agents when run on a 575F panel made from an 80–20 mixture of lard and chicken fat. Results indicated that steel wool performs well even when used on paper or sponge backings. Silex on nylon and cloth showed essentially the same scouring efficiency, 51 and 30%, as was obtained in the previous studies. Steel wool was found to maintain its efficiency with usage, and silex bonded to nylon showed only a slight decrease with usage.

It is concluded that a testing method has been developed to measure the Scouring Efficiency of abrasive cleaners on a test panel by wearing away a tough fatty film. Results are based on comparisons with a set standard, and are best run by one person on a single test panel. Experimental work indicates the method may have value in other studies, such as efficiency after usage, and the effect of various supporting media for the abrasive proper.

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An Amperometric Titration Method for Bleach Evaluation

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Abstract

An analytical method has been devised as a rapid screening procedure which predicts how effective an active chlorine containing compound will be as a bleaching agent. The method is based on an amperometric titration which indicates bleaching performance from both the increase in whiteness and fabric tendering standpoints. Excellent correlation was obtained between amperometrically determined data and practical bleaching data for several extensively used bleaching agents. In connection with this amperometric titration method, a polarographic method is also presented which provides good correlation between the polarographically determined data and practical bleaching data.

Introduction

WITH THE AID of a newly developed amperometric titration method the bleaching performance of an active chlorine compound can be predicted. The procedure is based on a method suggested in the Operational Manual of Wallace and Tiernan, Inc. (7,8, 13). An E. H. Sargent Ampot Amperometric Titrator, equipped with a rotating platinum electrode and external saturated calomel electrode, is used. Good correlation between polarographically determined current readings and practical bleach tests has also been obtained.

All active chlorine compounds in aqueous solutions form hypochlorous acid by hydrolysis. The bleaching action of hypochlorous acid in solution may follow any of three types of reactions: chlorination, oxidation or chlorhydrination. At pH levels below 4, an appreciable portion of the available chlorine is present as free chlorine (9,10).

At higher pH levels, oxidation and chlorhydrination are the predominant reactions. Saturated compounds are oxidized, while unsaturated compounds are chlorhydrinated, thereby destroying the resonating structure of the molecule with a resulting loss of color (1).

Bleaching with hypochlorite solutions is seldom a reversible reaction. Some sources hold that bleaching is an oxidation reaction caused by oxygen liberated from hypochlorite (8–10).

Active chlorine compounds may be divided into two general groups. The first consists of the relatively simple inorganic hypochlorites. The second comprises the organic *N*-chloro compounds. When *N*-chloro compounds are dissolved in water (it should be noted that solubility is rather limited with most of the organic compounds), the *N*-Cl bond is partially hydrolyzed (3–5, 14):

$$RR'NCl + H_2O \rightleftarrows RR'NH + HOCl$$

The HOCl on the right side of the equation is referred to as free available chlorine, the RR'NCl on the left side of the equation is referred to as combined available chlorine.

The proposed method differentiates between the free available chlorine content and the combined available chlorine content of a solution. Differentiation of the two forms of available chlorine is based on the concept that *N*-chloro compounds (combined available chlorine compounds) are activated by potassium iodide in acid media (pH 4), while the free available chlorine compounds can be reduced in a neutral pH range (6.5–7.5) without potassium iodide present (7). Using the E. H. Sargent Ampot Amperometric Titrator, equipped with a Sargent Synchronous Rotator Platinum and a saturated calomel electrode pair, titration data were obtained for solutions containing a low concn of bleaching compound (usually 10 ppm total available chlorine). It was determined polarographically that an applied voltage of zero volts was the most suitable for our procedure.

Experimental

One hundred ml of a 10 ppm total available chlorine solution of bleach were placed in a cell and the pH adjusted to 7, using a mixed phosphate buffer. The electrodes were immersed in the solution and a reading was obtained from the ammeter at the zero applied voltage. This was identified with the initial free available chlorine content. The solution was titrated with a reducing agent, in this case a 0.00563 normal phenylarsene oxide solution, and the decreasing

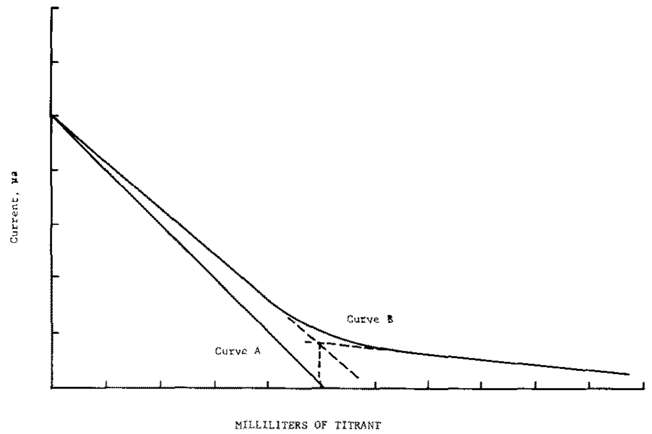

FIG. 1. Amperometric titration endpoint determinations.

TABLE I
Comparison of Amperometric Titration and Practical Bleaching Data

Compound	% Free available chlorine	% Increase in whiteness	
		pH 10; 160F	pH 7; 160F
Active chlorine containing compounds of major industrial use			
Sodium hypochlorite	100	14.5	14.6
Trichloroisocyanuric acid	94	9.1	10.7
Dichloroisocyanuric acid	89	8.3	10.4
1,3-dichloro-5,5-dimethyl hydantoin	50	3.2	6.0
N-chloro-*p*-toluene sulfonamide	11	0.2	4.4
Active chlorine containing compounds of experimental nature			
N,N'-dichloro-*N,N'*-dimethyl-*a,a'*-dichloro-malonamide	100	2.1	13.8
N,N'-dichloro-*N,N'*-bis (methane sulfonyl) ethylene diamine	100	0.0	6.3
N-chloro succinimide	44	0.2	6.4
N,N-dichloro-methane-sulfonamide	39	0.9	3.3
Chlorinated acetone-urea	17	3.7	4.6

ammeter readings recorded. Titrant was added until a zero deflection of the ammeter needle was obtained. This indicated that all free available chlorine had been titrated.

The solution pH was then adjusted to 4, using an acetate buffer and potassium iodide was added. If combined available chlorine is present the ammeter needle will deflect up scale. The deflection was recorded and designated as the combined available chlorine current. The solution was again titrated with phenylarsene oxide until a zero deflection was obtained on the ammeter. This indicated that all combined available chlorine had been titrated. The ml required for titration of the total available chlorine were obtained by adding the ml required for the free available and combined available chlorine titrations.

In cases where reactive compounds were titrated, a titration curve of free available chlorine such as A (Fig. 1) was obtained. The endpoint occurred at zero μ-amp. In these cases the pH was adjusted and KI added at this endpoint and the combined available chlorine titration was carried out. With less reactive compounds, a titration curve such as B (shown) was obtained. In this case it was necessary to run one titration and extrapolate to the endpoint. Then in the combination titration, the pH was adjusted and KI added at this point and the combined available chlorine titration continued.

An example of the type of tritration in which the free available chlorine endpoint must be determined as in B (shown) is as follows: Using 100 ml of a 10 ppm total available chlorine solution of 1,3-dichloro-5,5-dimethyl hydantoin, the pH was adjusted to 7 and an ammeter reading of 1.5 μ-amp was obtained. The addition of 0.00563*N* phenylarsene oxide caused a zero deflection to be obtained after 2 ml of titrant were added. The pH was then adjusted to 4, and 1 ml of a 0.1*N* solution of potassium iodide was added. This caused the ammeter needle to deflect up scale to 6 μ-amp. Titrant was again added until the endpoint obtained, at 4 ml. A plot of this data is shown in Figure 2. Due to differences in solubility and stability, solutions of the compounds studied were made and allowed to stand for one hour. Titration data was then obtained on these solutions.

As implied earlier, the free available chlorine or hypochlorous acid functions as the bleaching agent and as it is exhausted, generally more is supplied by the combined available chlorine. We have found that by determining the ratio of free available chlorine to the total available chlorine the effectiveness of an active chlorine containing compound can be predicted. Calculation of percentage free available chlorine is as follows:

$$\begin{array}{l} \%\ \text{Free} \quad \text{ml of titrant to obtain} \\ \text{Available Cl}_2 = \text{free available Cl}_2\ \text{endpoint/total} \\ \qquad\qquad \text{ml of titrant} \times 100 \end{array}$$

This prediction has been verified, in a majority of the cases, by comparing the data obtained amperometrically to data obtained from a practical bleach test. The practical test data was obtained at both pH 7 and 10, at 160F, in a Launder-Ometer (L-O-M). The procedure used is as follows: 200 ml of a 100 ppm total available chlorine solution were heated to

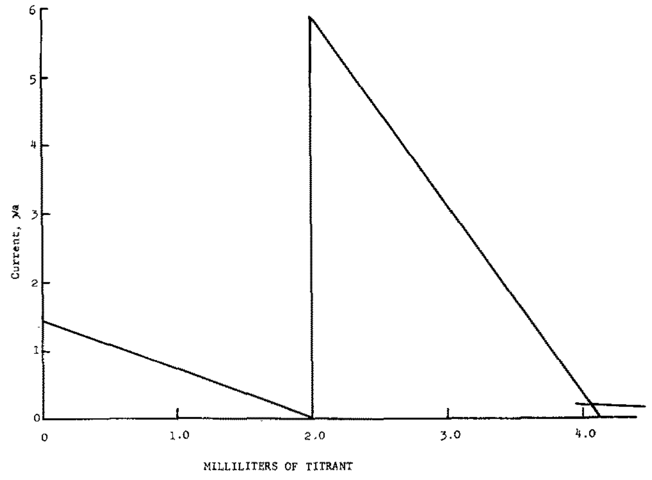

FIG. 2. Amperometric titration plot.

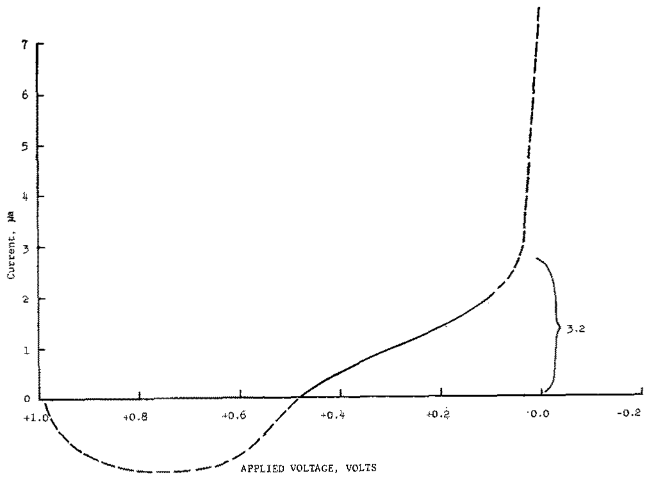

FIG. 3. Polarogram of active chlorine compound.

TABLE II

Correlation Between Practical Bleaching and Amperometric Titration Data

Compound	% Free available chlorine	% Increase in whiteness pH *10, 160F*	% Tensile strength loss
Sodium hypochlorite	100	14.5	83
Trichloroisocyanuric acid	94	9.1	86
1,3-dichloro-5,5-dimethyl hydantoin	50	3.2	56

160F in a pint L-O-M jar; pH was adjusted to either 7 or 10 using phosphate or carbonate buffers, respectively; 14 g of fabric consisting of two 4 in. x 4 in. squares of unbleached muslin, twelve 2.5 in. x 3.5 in. swatches of Pure Finish Indianhead muslin and fifteen .25 in. stainless steel balls, were added to the pint jar, which was then capped and placed in the L-O-M preheated to 160F. The L-O-M, rotating at 42 rpm was run for 10 min, after which time the swatches were rinsed in demineralized water, hydroextracted and pressed. Initial and final reflectances of two unbleached muslin swatches were determined on a Hunter Reflectometer using the blue filter. From these data, percentage increase in whiteness was calculated. This is the value which is reported in Table I.

Excellent correlation is evident with respect to data for active chlorine containing compounds of major industrial use. A Product Moment Correlation Coefficient of 0.928 has been obtained for this data (12). This correlation was lost, however, when dealing with experimental compounds and can be explained by the fact that these compounds were quite impure. It does point out, in any event, how the amperometric method is suitable as a rapid screening procedure.

Practical bleaching was conducted at pH between 9 and 10, while the amperometric data was obtained at pH 7. Attempts to improve correlation of data were made by obtaining practical bleaching data at pH 7. Although correlation was still excellent for the industrially used compounds only slight improvement was found for the experimental type compounds. Based on the results for the industrially used compounds, further attempts were made to obtain amperometric data at pH 10. All attempts failed, however, due to shifts in the reduction potential and nonstoichiometry.

It should be pointed out at this time that this type of amperometric titration also gives an indication of the potentially hazardous nature of an active chlorine containing compound with respect to fabric tendering. Tensile strength losses are attributable to the oxidizing agent, in this case the free available chlorine (hypochlorous acid) content of the compound. Practical experience indicates that sodium hypochlorite damages fabric to a greater extent than does, for example, 1,3-dichloro-5,5-dimethyl hydantoin or *N*-chloro-*p*-toluene sulfonamide. By determining amperometrically, the free available chlorine to total available chlorine ratio of an active chlorine containing compound, one is able, not only, to predict the bleaching effectiveness of the compound in question, but also its tendencies towards damaging fabric. Table II shows the correlation between amperometric data, practical bleaching data and tensile strength loss data. It is worth mentioning here, that although 1,3-dichloro-5,5-dimethyl hydantoin does not show quite as high bleaching effectiveness, the fact that its fabric tendering properties are considerably lower than the other two compounds, makes this compound desirable as a bleaching agent (2,11).

TABLE III

Practical Bleaching and Polarographic Current Data

Compound	% Increase in whiteness pH 10, 160F	Polarographic current data pH 10, μa
Sodium hypochlorite	14.5	10.4
Trichloroisocyanuric acid	9.1	9.5
Dichloroisocyanuric acid	8.3	5.2
1,3-dichloro-5,5-dimethyl hydantoin	3.2	3.2
N-chloro-*p*-toluene sulfonamide	0.6	0.4
N,*N'*-dichloro-*N*,*N'*-dimethyl-α,α'-dichloro-malonamide	2.1	5.3
Chlorinated acetone-urea	3.7	1.9
N-chloro succinimide	0.2	0.0

Although attempts to titrate amperometrically at pH 10 proved unsuccessful, polarographically determined current data at pH 10 showed marked correlation ($r = 0.901$) with practical bleaching data obtained at the same pH. Data are reported in Table III. The polarographic data were obtained by measuring the current at zero applied voltage on a polarogram of the compound. An E. H. Sargent Model XXI Polarograph, equipped with rotating platinum and saturated external calomel electrode pair, was used for these determinations. An example of this type of determination is shown.

It must be conceded, however, that polarographically determined data, using a rotating platinum electrode, are not completely reproducible. The basic drawback to this empirical method is that a compound cannot be evaluated and compared to previously obtained data. Due to the irreproducibility, all of the compounds would have to be re-evaluated each time a new compound was investigated. The data obtained and presented do, however, add strength to the amperometrically determined values.

The amperometric procedure presented appears to have potentialities as a rapid screening procedure. By means of a five-minute titration one can obtain a general picture of an active chlorine containing compound with respect to its bleaching characteristics. If, after an amperometric titration, it is found that a particular compound shows good qualities as a bleaching agent, it can be tested further by means of standard practical bleaching and tensile strength procedures. We have strived to show the bleaching characteristics of a compound can be determined with a procedure other than the conventionally used methods. Attempts have been made by previous workers to show a correlation between bleaching and oxidation potentials, but these generally have not been successful. The correlation among the data presented in this paper, however, indicates that these methods, for predicting bleaching effectiveness, warrant further investigation.

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